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# BEHAVIOR OF ALUMINUM IN SOLID PROPELLANT COMBUSTION.

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## ABSTRACT

The usefulness of powdered aluminum as a propellant ingredient is compromised by the details of its behavior in the combustion zone, its combustion in the motor volume, and by the nature of the product oxide droplets. This project was aimed at clarification of the mechanisms governing concentration, sintering and agglomeration of aluminum on the propellant burning surface, subsequent combustion of agglomerated aluminum, and resulting size distribution of the $Al_2O_3$ product droplets.

The approach was to study the response of individual propellant ingredients, and combinations, to controlled heating in laboratory experiments such as hot stage microscope and hot plate apparatus. This was followed by combustion and quench tests on combinations of ingredients (e.g., dry-pressed aluminum-ammonium perchlorate mixtures). This involved high speed combustion photography, and scanning electron microscope studies of quenched surfaces. Exploratory tests were also made on propellants, including quench burns, burning under liquid nitrogen, combustion photography of the aluminum droplet burning history, and quench-collection of condensed material from different distances from the burning surface. These exploratory tests were done at atmospheric pressure.

Results suggest the relative roles of binder, aluminum and oxidizer in accumulation and agglomeration of aluminum on the burning surface; the role of the diffusion flame on ignition of aluminum; and the nature of the agglomerate combustion and its role in determining oxide droplet size. Several binders and aluminum sources were examined in the controlled heating studies. More extensive systematic variation of ingredients is planned for the tests on combustion of ingredient combinations, and the propellant test methods need to be adapted to use at elevated pressure.

# BEHAVIOR OF ALUMINUM IN SOLID PROPELLANT COMBUSTION

## INTRODUCTION

The powdered aluminum used as an ingredient in solid propellants behaves in a way quite unlike other propellant ingredients. Thus aluminum not only modifies the usual propellant burning characteristics, but introduces new characteristics, such as burning droplets in the combustor flow. This has forced detailed consideration of the aluminum behavior, in order to minimize the guess work in propellant formulation and motor design. Early studies focused on the mechanism of burning of single aluminum droplets in simple atmospheres. These studies left many questions unanswered about the effect of the combustion environment (chemistry, pressure, etc.). Even more important, propellant studies showed that a complex process of accumulation - agglomeration of aluminum particles occurred on the propellant burning surface, that dictated the size, purity and burning time of the aluminum droplet in the gas flow in the rocket motor. This in turn affected combustion and nozzle efficiency, combustor stability, and component erosion.

The present study was aimed at clarifying the processes governing the aluminum agglomeration and combustion, so that something more than empirical methods could be applied to predicting, controlling and changing aluminum behavior and its effects on motor behavior.

## TECHNICAL APPROACH

The approach was to determine how the <u>individual</u> ingredients of a propellant behave under controlled heating; then how various ingredient combi-

nations behaved, and then how the full combination behaved. The experiments ranged from well controlled, but low heating rate tests to combustion and quench tests, as follows:

1. Controlled heating in a hot stage microscope, giving controlled atmospheres and favorable observational conditions (heating rate limited to about $10^{o}C/sec$, up to $1400^{o}C$).

2. Rapid heating in a controlled atmosphere by dropping samples on a preheated plate (heating rate 100 - $1000^{o}C/sec$, sample observation primarily by pre- and post-test examination).

3. Combustion and quench experiments providing real combustion zone conditions with observation by combustion photography and electron microscope studies of pre- and post-test samples.

4. Efforts were made to control the microstructure of the heterogeneous test samples in a way that would facilitate interpretation of test results.

This test strategy (1 - 4) was based on accumulated experience that had already established the qualitative aspects of aluminum behavior and posed many hypotheses and debates about the mechanisms involved. It seemed unlikely that the past experience could be translated into useful understanding or systematic application unless underlying processes could be observed under simpler and more controlled conditions such as in 1 - 4 above.

## PREVIOUS REPORTING

Most of the work on this project has been published in References 1 and 2, and will not be repeated here. The material covered here consists of work done between 1 August and 30 September 1977, and a tabulation of

results and conclusions from the overall project.

PROGRESS FOR AUGUST, SEPTEMBER 1977

Several studies were in progress after the last report (Ref. 2). These were oriented towards a) supplementing previous work on ingredient behavior, b) exploring new approaches to controlled experiments and systematic control of variables, and c) looking further in the progression of aluminum behavior, i.e., towards detachment, ignition and combustion of agglomerates.

Binder Response to Heating - PBAN

The study of binder response to heating previously reported in Reference 1 has been expanded to include PBAN (polybutadiene-acrylonitrile). A comparison of the thermal decomposition of five binders (PS, PBAA, CTPB, HTPB, and PBAN) in air, oxygen and argon is presented in Figure 1. The details of the decomposition of the first four binders was described in Reference 1. PBAN behaves in a similar manner with gradual discoloration, light outgassing at about 240°C, and vigorous boiling at about 420°C. One unusual aspect of PBAN is the sudden appearance of cracks or chips running parallel to the heating surface at a temperature of 380°C. It is believed that this phenomenon is similar to the "encapsulated bubbles" observed in HTPB. Because of the elasticity of HTPB, gases trapped in the binder during mixing and curing expand slowly and form spherical voids in the binder in the temperature range 300 - 500°C. PBAN appears to be more brittle than HTPB and the pressure of the trapped gas causes the binder to crack abruptly along surfaces which appear to be parallel to the heating surface.

Granular Solid Binders

Composite solid propellants of interest in this research include two or more granular solid ingredients -- AP, aluminum, and possibly burning rate modifiers such as $Fe_2O_3$ -- all encapsulated in a rubber-like polymeric binder. In addition to its role as a fuel, this binder provides a castable medium which holds the ingredient powders in a polydisperse matrix. During combustion, the binder forms a sticky melt layer which further enhances the retention of aluminum to the surface. These binders consist of three or more ingredients which are often quite difficult to mix in correct proportions in small quantities. Further, the blending of a high percentage of solid powders to binder is very difficult, requiring a considerable amount of time both for mixing and curing. The granular powders (AP, Al) can be compressed into a solid pellet in a hydaulic press but the effect of a sticky melt layer of binder on the retention of aluminum at the surface is eliminated. It is therefore advantageous to seek a granular powder which will melt and exhibit a combustion behavior similar to standard polymeric binders.

Previous investigators[3] have used powdered carnauba wax to represent the binder in pressed samples. Heating of carnauba wax in the hot-stage microscope revealed thermal decomposition similar to standard rubber-like binders, although at substantially lower temperatures, with melt at 80°C followed immediately by vigorous boiling. Heating in air and argon leaves only a thin, clear slick residue at 600°C, while heating in oxygen usually results in ignition. Pressed mixtures of Al and wax were heated in the hot-stage microscope and again revealed behavior similar to the results of Al-binder heating reported in Reference 1. Heating in air and argon pro-

duced a small number of very large agglomerates while heating in oxygen yielded ignition leaving a slightly sintered filigree of aluminum.

A pellet of 15% wax - 15% H-30 aluminum - 70% AP was pressed, cut into a 2x10x10 mm sample, ignited in the combustion bomb at 1000 psi and quenched by rapid depressurization. When viewed in the scanning electron microscope, the quenched surface was found to have a substantially larger amount of melted binder than a quenched sample containing 15% PBAN - 15% Al - 70% AP. The surfaces do exhibit a substantial degree of similarity and it is anticipated that propellants pressed with a smaller percentage of wax will provide burning surfaces with melt regions similar to standard propellants.

Techniques to Study Agglomeration, Detachment, Ignition and Combustion

Tests directed towards gaining insight into the behavior of aluminum (accumulation - agglomeration) on the surface of a burning propellant included still 35 mm photography and 16 mm high speed motion picture photography at atmospheric and rocket motor pressures, quenching of propellants by rapid depressurization from motor pressures, and quenching at atmospheric pressure by cold jet impingement and by burn-out of thin samples on surfaces with high and low heat conductivities. All quenched samples were subsequently examined under the scanning electron microscope. Much of this work has been reported in AFOSR contractors meetings and in Reference 2.

Finally, development of experiments attempting to trace the burning history of aluminum after leaving the burning surface was initiated. Burning aluminum was quenched in the immediate vicinity of the burning surface by immersing the burning propellant in liquid nitrogen and was quenched at greater distances from the burning surface by directing the plume into a

pool of ethanol. Scanning electron micrographs of the residual aluminum have been presented in Reference 2. Methods of photography of burning agglomerates later in their burning history were explored, with the objective of circumventing the problems of high velocity and smoke obscuration.

## RESULTS AND CONCLUSIONS

Results of this research have established a number of attributes of behavior of aluminum that explain its behavior in propellant combustion, as well as behavior of other propellant ingredients that is important to aluminum behavior. These are summarized below as separate items that go together to explain the unique aspects of aluminum behavior in propellant combustion. In many cases the results reinforce earlier interpretations, and in some cases reflect new mechanistic arguments.

1. Properties of Individual Aluminum Particles:

a) Aluminum particles used in propellants are usually of irregular shape, with rough surface, and about 99% purity.

b) They characteristically have an oxide "skin" of about 0.05 μm thickness, whose presence is critical to chemical stability of the particle.

c) When heated, the particles do not change appreciably until they reach about $400^{o}C$ + .

d) The aluminum is presumably expanding with heating, and should put the oxide skin under stress because of its lesser thermal expansion coefficient.

e) It is probable that the oxide is a hydrate, which may lose water during heating.

2. Near the Aluminum Melting Point, Response of Particles to Heating Begins, is typified by:

a) Enlargement or spheroidization of the particle.

b) Appearance of "warts" of aluminum on the particle due to expansion through flaws in the oxide.

c) Evidence of wrinkling of the oxide skin after heating to above the aluminum melting point and cooling (indicative of inelastic stretching of the oxide).

d) Resistance of some particles to visible change due to heating, especially in oxygen atmospheres.

3. Comparison of Aluminum Powders:

a) Typical powder samples contain a myriad of particle shapes and sizes.

b) A range of grades are available giving different size distributions. This is usually accompanied by different particle shapes and/or oxide skin characteristics.

c) Different grades have entirely different responses to heating. The quality controls of manufacturers are not usually motivated by rocket combustion problems.

4. Heating of Aluminum Powders Above the Melting Point:

a) Leads to various degrees of coalescence of particles, referred to as "agglomeration." Different powders differ in their degree of agglomeration.

b) Agglomeration leads to coalescence of hundreds of particles. Acid etching of agglomerates after tests shows large scale crystal structure indicative of exclusion of oxide fragments during coalescence.

c) Presence of an oxidizing atmosphere impedes coalescence, causes instead a sintering process in which oxidized connections form among particles.

d) Pretreating of aluminum particles, by heating to above the melting point and cooling, drastically reduces the tendency to agglomeration or sintering of powders. This behavior is believed to be due to previous inelastic stretching of the oxide skin which allows it to accomodate subsequent reexpansion of the aluminum without failure or "leaking". (The pre-stretched skins are wrinkled, and apparently simply "unwrinkle" when stretched.)

e) Experiments using a preheated plate on which powders are dropped indicate that the response of powders to heating is not critically dependent on heating rate, supporting the view that hot stage microscope tests are relevant to aluminum behavior at the higher heating rates in the propellant combustion zone.

5. Heating Tests on Propellant Binders Showed That:

a) Conventional binders start decomposing around 300°C.

b) A melt-like state exists in the temperature range 420 to 600°C.

c) A dry residue develops at about 600°C.

d) In oxygen, ignition usually interrupts the process at around 600°C.

e) Polysulfide binder exhibited the above sequence of behavior at about 200°C lower temperatures.

f) HTPB binder, and CTPB to a lesser extent, exhibit a clear liquid product in the temperature range 950 to 1100°C when heated in oxygen.

6. Heating Aluminum-Filled Binders Exhibited the Following Behavior:

a) The binders behaved much as they did without aluminum present.

b) At the temperatures where aluminum sintering normally occurred with aluminum powder alone, binder residues enhanced cohesion of the powders,

and individual particles were found to be coated and interconnected by binder ( 660°C).

c) In non-oxidizing atmospheres, extensive agglomeration of aluminum occurred when 50/50 binder/aluminum samples were heated to 1000°C.

d) Ignition of samples occurred in oxygen with all binders except PS.

7. <u>Combustion of Pressed Mixtures of AP-Al Powders</u>:

a) Solid samples made by pressing 85/15 mixtures of ammonium perchlorate and aluminum were burned, and quenched by rapid depressurization.

b) Samples made from AP and Al powders of 100 μm particle size did not show evidence of agglomeration on the quenched surface.

c) Samples made from 100 μm AP and 15 μm Al showed extensive retention and agglomeration of aluminum. Thus the AP flame apparently does not ignite aluminum readily, while the surface does have "adhesive" properties.

d) Further systematic testing is planned, with particle size, mixture ratio, and pressure as variables.

8. <u>The State of the Propellant Burning Surface</u> was observed by study of quenched samples (quenches by rapid depressurization, by impingment of a freon jet, and by burnout on a quench plate).

a) Aluminum is accumulated, and with UTP 3001 it is accompanied by an accumulation of "molten" binder.

b) The distribution of accumulated aluminum reflects original distribution in the propellant, in an array around the oxidizer particles.

c) This sintered array apparently breaks down and coalesces into agglomerates in a manner reflecting details of the retention forces,

interconnectedness, and encroachment of diffusion flamelets, all of which change progressively as burning proceeds (on the microscopic scale).

9. Burning a Propellant Under Liquid Nitrogen:

a) UTP 3001 (Titan III C) propellant will burn at one atmosphere under $LN_2$.

b) The aluminum agglomeration process is interrupted at various stages, providing samples for study.

c) Scanning electron microscope (SEM) studies of the collected material showed large spherical aluminum agglomerates with oxide lobes.

d) SEM studies showed also near-spherical agglomerates with local open areas on the surface revealing partially consolidated constituent particles inside, indicating that agglomeration is a complicated, surface-tension driven process.

e) SEM studies showed also sintered assemblages of particles. Acid etching to remove aluminum left a "skeleton" of interconnected oxide shells, with the interconnections consisting of hollow tubes.

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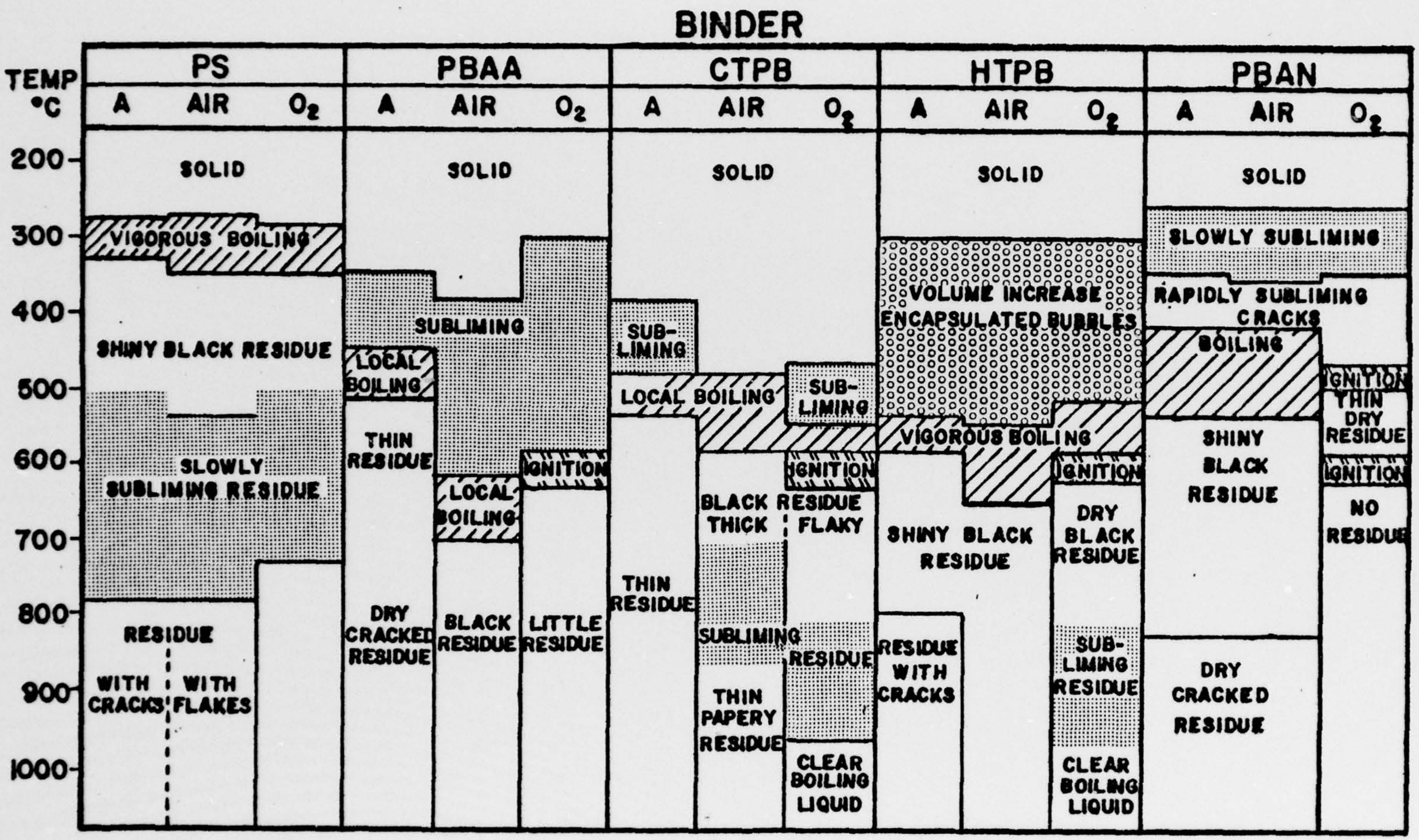


Figure 1. Thermal Decomposition of Binders

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The usefulness of powdered aluminum as a propellant ingredient is compromised by the details of its behavior in the combustion zone, its combustion in the motor volume, and by the nature of the product oxide droplets. This project was aimed at clarification of the mechanisms governing concentration, sintering and agglomeration of aluminum on the propellant burning surface, subsequent combustion of agglomerated aluminum, and resulting size distribution of the $Al_2O_3$ product droplets. The approach was to study the response of individual propellant ingredients, and combinations, to controlled heating in laboratory experiments such as hot stage microscope and hot plate apparatus. This

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